

Specification

A composite carrier of catalysts for propylene polymerization, a catalyst component and a catalyst comprising the same

Cross Reference of Related Application

The present application claims priority Chinese Patent Application No. 03105214.2, filed on February 24, 2003, and Chinese Patent Application No. 03153662.X, filed on August 20, 2003, which are incorporated in here by reference in their entirety and for all purposes.

Technical field

The present invention relates to a composite carrier of catalysts for olefin polymerization, in particular for propylene polymerization, to catalyst components and catalysts comprising the same.

Technical background

It is well known that high activity supported type of Ziegler-Natta catalysts have been broadly used in homopolymerization of ethylene or propylene, and copolymerization of ethylene or propylene with other alpha-olefins. In the disclosed patent techniques, high activity supported catalysts typically utilize magnesium chloride as single carrier. In order to enhance catalytic activity, magnesium chloride carrier is prepared by various physical or chemical processes at first, and then a transition metal compound and optionally an electron donor compound are supported on said carrier to form catalytic active center. This type of catalysts can be classified as particulate (non-spheric) catalyst and spheric catalyst in terms of particle morphology. US4784983 and US4861847 disclose a particulate

catalyst, which is obtained by preparing particulate essentially consisting of magnesium chloride through dissolving-coprecipitating process, and then treating said particulate with a titanium halide and an electron donor compound. When used in olefin polymerization, especially in propylene polymerization, said catalyst exhibits high polymerization activity and stereospecificity. However, due to the limitation of particle morphology of the catalyst, it is very difficult to obtain high impact resistant copolymer having high ethylene content when the catalyst is used in propylene copolymerization. This is a common characteristic of this type of particulate catalysts. EP0395083 discloses a catalyst for olefin polymerization, which is a high activity spheric catalyst obtained by preparing a magnesium chloride-alcohol-adduct spheric carrier through a reaction of magnesium chloride and an aliphatic alcohol, and then supporting a titanium halide and an electron donor compound on said spheric carrier. When used in propylene polymerization, this spheric catalyst exhibits high activity and stereospecificity, and obtained polymer particles have good morphology. The catalyst can be used to prepare high impact resistant ethylene-propylene copolymer having high ethylene content. However, since this kind of catalysts generally have a large particle size, breaking phenomenon is likely to occur during polymerization. This is especially true when prepolymerization times is lower. Thus produced polymer fines will affect stable operation of a polymerization unit.

Another type of catalysts are those olefin polymerization catalysts obtained by loading magnesium chloride on porous inorganic oxide support such as silica and the like to form a composite carrier, and then treating the composite carrier with a titanium halide and an electron donor compound. For example, GB2028347 discloses a process for preparing a catalyst component supported on porous inorganic oxide support, namely, impregnating silica support with magnesium chloride solution, then evaporating solvent, and reacting thus obtained solid product with a transition metal compound, in particular a titanium compound. For another example, CN1035186C discloses a technique for preparing high activity

polypropylene catalysts utilizing silica support, wherein the catalyst product is obtained by dispersing porous silica support having hydroxyl on surface thereof in a solution of magnesium chloride in tetrahydrofuran, drying said suspension to form a $MgCl_2/SiO_2$ composite carrier, and then treating said carrier with titanium tetrachloride and an electron donor compound. Said catalysts exhibit, however, lower activity. For instance, when diisobutyl phthalate is used as internal electron donor, 2 hours polymerization activity of said catalyst in propylene polymerization is at most 20kgPP/gCat. Such technique for preparing composite carrier type of catalysts through impregnating process is also disclosed in many other patents, for example, US5559071, US5625015, WO94/14855, WO94/14856, WO95/11263, WO95/15216, WO95/12622, WO96/16093, WO96/05236, WO97/23518, WO98/01481, WO99/46306, WO00/22011, WO00/40623, WO00/05277 and EP0295312.

However, when used in propylene polymerization, the catalysts prepared using the carrier obtained by above-described process of impregnating silica with magnesium chloride solution exhibit unsatisfied polymerization activity. The reason maybe lies in that such impregnation process controls particle morphology of final catalyst substantially utilizing particle morphology of silica support itself. Since the porous silica support commonly used has a large average particle size, typically about 50 microns, loading amount of active component on said silica support is limited so that the final catalyst exhibits a lower activity.

US4376062 discloses a composite carrier catalyst, which is a catalyst having an average particle size of about 25 microns obtained by contacting anhydrous magnesium chloride with titanium tetrachloride in an electron donor solvent, such as tetrahydrofuran, to react each other to form a slurry or a solution containing active component, then mixing said slurry or solution with fumed silica having an average particle size of from 0.007 to 0.05 microns and spray drying. When used in ethylene polymerization after reacting with an activator (alkyl aluminium), said catalyst exhibits higher polymerization activity. However, for the purpose of use in

propylene polymerization, addition of internal electron donor is necessary in order to obtain polypropylene having high isotacticity, while above-described preparation process is not in favor of stably controlling the composition of individual component on the carrier. In addition, since a large amount of titanium tetrachloride occurs in the slurry to be spray dried, the spray dryer is likely to be eroded, and this goes against industrial production.

Summary of the invention

One object of the invention is to provide a composite carrier of catalysts for propylene polymerization, comprising magnesium halide and silica material with an average particle size of less than 10 microns.

Another object of the invention is to provide a composite carrier of catalysts for propylene polymerization, which is spheric particles obtainable by contacting magnesium halide with one or more electron donor compounds to form a solution, then mixing the solution with silica material having an average particle size of less than 10 microns to form a mixture, and drying the mixture through spray drying process.

Still another object of the invention is to provide a catalyst component for propylene polymerization, comprising reaction product of the composite carrier according to the present invention and a titanium compound represented by formula $Ti(OR^2)_{4-m}X_m$, in which R^2 groups are identical or different, and are C_{1-14} aliphatic hydrocarbyl, X are selected from the group consisting of F, Cl, Br and mixture thereof, m is an integer of from 1 to 4, wherein prior to, during, or after the reaction between the composite carrier and the titanium compound, the composite carrier is treated using an internal electron donor compound.

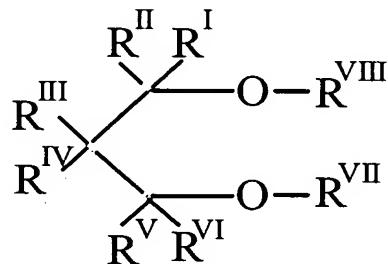
Still another object of the invention is to provide a catalyst component for propylene polymerization, which is obtainable through a process comprising the steps of:

(i) preparing spheric composite carrier by contacting magnesium halide with one or

more electron donor compounds to form a solution, then mixing the solution with silica material having an average particle size of less than 10 microns to form a mixture, and drying the mixture through spray drying process;

(ii) reacting the composite carrier prepared in step (i) with a titanium compound represented by formula $Ti(OR^2)_{4-m}X_m$, in which R^2 groups are identical or different, and are C_{1-14} aliphatic hydrocarbyl, X are selected from the group consisting of F, Cl, Br and mixture thereof, m is an integer of from 1 to 4, and

(iii) prior to, during, or after the reaction between the composite carrier and the titanium compound, treating the composite carrier with an internal electron donor compound selected from the group consisting of esters of aliphatic polycarboxylic acid, esters of aromatic carboxylic acid, and 1,3-diether compounds having a general formula (I)



(I)

in which R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are identical or different, and are selected from the group consisting of hydrogen, halogen, optionally halogenated linear or branched $C_{1-C_{20}}$ alkyl, optionally halogenated $C_{3-C_{20}}$ cycloalkyl, optionally halogenated $C_{6-C_{20}}$ aryl, optionally halogenated $C_{7-C_{20}}$ alkaryl and optionally halogenated $C_{7-C_{20}}$ aralkyl, R^7 and R^8 are identical or different, and are selected from the group consisting of optionally halogenated linear or branched $C_{1-C_{20}}$ alkyl, optionally halogenated $C_{3-C_{20}}$ cycloalkyl, optionally halogenated $C_{6-C_{20}}$ aryl, optionally halogenated $C_{7-C_{20}}$ alkaryl and optionally halogenated $C_{7-C_{20}}$ aralkyl, and $R^1 - R^6$ groups can be bonded each other to form a ring, and mixture thereof.

Still another object of the invention is to provide a catalyst for propylene polymerization, comprising reaction product of the solid catalyst component

according to present invention, an alkyl aluminium compound and optionally, an external electron donor component.

When used in olefin polymerization, in particular in propylene polymerization, the catalysts according to the present invention exhibit high activity and high stereospecificity, and can be used to prepare high impact resistant ethylene-propylene copolymer having high ethylene content.

Detailed description of the invention

In the first aspect, the present invention provides a composite carrier of catalysts for propylene polymerization, comprising magnesium halide and silica material with an average particle size of less than 10 microns. Said composite carrier is spheric particles obtainable by contacting magnesium halide with one or more electron donor compounds to form a solution, then mixing the solution with silica material with an average particle size of less than 10 microns to form a mixture, and drying the mixture through spray drying process.

Magnesium halides useful in the present invention can be represented by formula $Mg(OR^1)_{2-m}X_m$, in which R^1 are identical or different, and are linear, branched or cyclic alkyl having 1 to 14 carbon atoms, X are selected from the group consisting of F, Cl, Br and mixture thereof, and m is 1 or 2. Examples include, but are not limited to, magnesium dichloride, magnesium dibromide, magnesium phenoxide chloride, magnesium isopropoxide chloride, magnesium butoxide chloride, and the like, with magnesium dichloride being preferred. The magnesium halide can be used alone or in combination.

Suitable electron donor compounds useful to dissolve the magnesium halide include optionally halogenated aliphatic or aromatic alcohols, aliphatic ethers, cyclic ethers, aliphatic ketones, alkyl esters of aliphatic or aromatic carboxylic acid. Optionally halogenated saturated aliphatic alcohol having from 1 to 8 carbon atoms; lower alkyl ester of saturated aliphatic carboxylic acid having from 1 to 4 carbon atoms; lower alkyl ester of aromatic mono- or poly-carboxylic acid having from 7

to 8 carbon atoms; aliphatic ether having from 2 to 8, preferably from 4 to 5 carbon atoms; cyclic aliphatic ether having from 4 to 5 carbon atoms, preferably monoether or diether having 4 carbon atoms; and aliphatic ketone having from 3 to 6, preferably from 4 to 5 carbon atoms are especially suitable. The term "lower alkyl" as used herein intends to mean alkyl having from 1 to 6 carbon atoms.

Preferably, the electron donor compound is a system comprising at least one of optionally halogenated C₁₋₈ aliphatic alcohols and optionally halogenated C₇₋₁₀ aromatic alcohols. More preferably, the electron donor compound is at least one of optionally halogenated C₁₋₈ aliphatic alcohols and optionally halogenated C₇₋₁₀ aromatic alcohols, or a mixture of said alcohol with a C₁₋₆ aliphatic ether, a C₃₋₅ cyclic ether, or a C₁₋₆ alkyl ester of aliphatic or aromatic carboxylic acid.

Examples of the electron donor compound include, but are not limited to, methanol, ethanol, isopropanol, n-butanol, iso-butanol, iso-pentanol, n-octanol, iso-octanol, ethylene glycol, propylene glycol, chloroethanol, trichloroethanol, diethyl ether, dibutyl ether, methyl formate, ethyl acetate, butyl acetate, dihexyl ether, tetrahydrofuran (THF), acetone, methyl isobutyl ketone, ethyl benzoate, diethyl phthalate, di-n-butyl phthalate, di-iso-butyl phthalate, and the like, with ethanol, isopropanol, n-butanol, trichloroethanol, THF, ethyl benzoate, and diethyl phthalate being preferred. The electron donor can be used alone or in combination.

Suitable electron donor compounds also include those systems comprising an organic epoxy compound and/or an organo phosphorus compound. The organic epoxy compound is at least one selected from the group consisting of aliphatic epoxy compound or diepoxy compound, halogenated aliphatic epoxy compound or diepoxy compound, and glycidol ether, having from 2 to 8 carbon atoms. Examples include epoxy ethane, epoxy propane, epoxy butane, vinyl epoxy ethane, butadiene dioxide, epoxy chloropropene, glycidyl methyl ether, and diglycidyl ether. The organo phosphorus compound is selected from the group consisting of C₁₋₁₀ hydrocarbyl or C₁₋₁₀ halohydrocarbyl esters of phosphoric acid or phosphorous acid. Examples include trimethyl phosphate, triethyl phosphate, tributyl phosphate,

triphenyl phosphate, trimethyl phosphite, triethyl phosphite, tributyl phosphite, tribenzyl phosphite.

In order to react the magnesium halide with the electron donor to form a homogeneous solution, per mole of the magnesium halide needs typically from 3 to 50 moles, preferably from 6 to 30 moles of the electron donor compound. Such solution can be prepared in presence of an inert organic solvent, which does not form an adduct with the magnesium halide. Said inert solvent is preferably C₅₋₁₂ alkane, C₁₋₆ halohydrocarbon, or C₆₋₁₂ aromatic hydrocarbon, such as, hexane, heptane, dichloroethane, toluene, xylene, and ethyl benzene, and the like.

In order to obtain composite carrier having less particle size through spray drying, the silica material selected is typically silica having an average particle size of less than 10 microns, preferably less than 5 microns, and more typically fumed silica having an average particle size of less than 1 micron. This kind of silica has typically a specific surface area of 150 to 250 m²/g.

A slurry suitable for spray drying can be obtained by mixing said solution and said silica. In general, silica is added in an amount of from 10 to 200 grams of silica per liter of the solution.

Spray drying can be carried out as follows: performing spray drying by passing, together with an inert drying gas, the slurry obtained by mixing said solution and said silica material through a spray dryer, to obtain spheric solid particles.

In order to apply the composite carrier according to the present invention more well to prepare catalysts for propylene polymerization, it is generally desired that said composite carrier is spheric particles having an average particle size of from 5 to 60 microns, preferably from 10 to 40 microns, and more preferably from 12 to 30 microns.

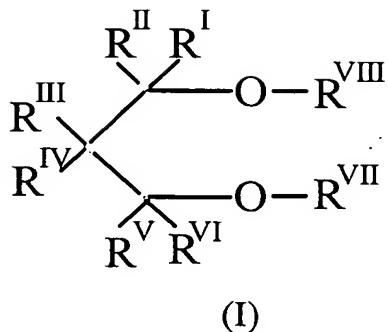
In the second aspect, the present invention provides a catalyst component for propylene polymerization, comprising reaction product of the composite carrier described above and a titanium compound represented by formula Ti(OR²)_{4-m}X_m, in

which R² groups are identical or different, and are C₁₋₁₄ aliphatic hydrocarbyl, X are selected from the group consisting of F, Cl, Br and mixture thereof, m is an integer of from 1 to 4, wherein prior to, during, or after the reaction between the composite carrier and the titanium compound, the composite carrier is treated with an internal electron donor compound.

Specifically, the titanium compound can be one or more selected from the group consisting of titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, tetrabutyl titanate, tetraethyl titanate, triethoxy titanium chloride, diethoxy titanium dichloride, ethoxy titanium trichloride, and titanium trichloride, with titanium tetrachloride being preferred. The titanium compound should be miscible in an apolar solvent at the application temperature.

Various internal electron donor compounds known in the art can be used to treat the composite carrier. Suitable internal electron donor compounds include esters of aliphatic polycarboxylic acid, and esters of aromatic carboxylic acid, for example, phthalates, malonates, succinates, glutarates, pivalates, carbonates, and the like. Examples include diethyl malonate, dibutyl malonate, diethyl 2,3-diisopropylsuccinate, diisobutyl 2,3-diisopropylsuccinate, di-n-butyl 2,3-diisopropylsuccinate, dimethyl 2,3-diisopropylsuccinate, diisobutyl 2,2-dimethylsuccinate, diisobutyl 2-ethyl-2-methylsuccinate, diethyl 2-ethyl-2-methylsuccinate, diethyl adipate, dibutyl adipate, diethyl sebate, dibutyl sebate, diethyl phthalate, diisobutyl phthalate, di-n-butyl phthalate, diisooctyl phthalate, diethyl maleate, di-n-butyl maleate, diethyl naphthalene dicarboxylate, dibutyl naphthalene dicarboxylate, triethyl trimellitate, tributyl trimellitate, triethyl hemimellitate, tributyl hemimellitate, tetraethyl benzene-1,2,4,5-tetracarboxylate, tetrabutyl benzene-1,2,4,5-tetracarboxylate, and the like.

In another embodiment of this aspect, prior to, during, or after the reaction between the composite carrier and the titanium compound, the composite carrier is treated with, as internal electron donor compound, at least one 1,3-diether compound having a general formula (I)



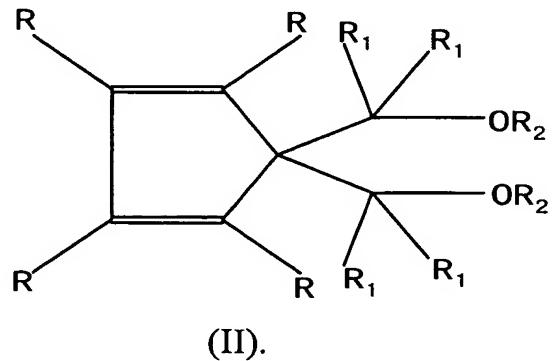
(I)

in which R^I , R^{II} , R^{III} , R^{IV} , R^V and R^{VI} are identical or different, and are selected from the group consisting of hydrogen, halogen, optionally halogenated linear or branched C_1 - C_{20} alkyl, optionally halogenated C_3 - C_{20} cycloalkyl, optionally halogenated C_6 - C_{20} aryl, optionally halogenated C_7 - C_{20} alkaryl and optionally halogenated C_7 - C_{20} aralkyl, R^{VII} and R^{VIII} are identical or different, and are selected from the group consisting of optionally halogenated linear or branched C_1 - C_{20} alkyl, optionally halogenated C_3 - C_{20} cycloalkyl, optionally halogenated C_6 - C_{20} aryl, optionally halogenated C_7 - C_{20} alkaryl and optionally halogenated C_7 - C_{20} aralkyl, and R^I - R^{VI} groups can be bonded each other to form a ring.

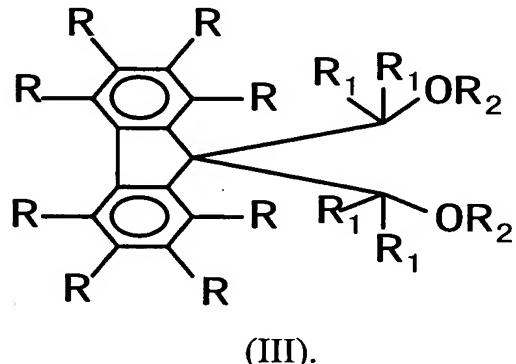
When used in propylene polymerization, the catalysts comprising an 1,3-diether compound having the general formula (I) as internal electron donor compound exhibit high polymerization activity, good response to hydrogen, and high stereospecificity, and obtained polymer powders have a large bulk density. Even if no external electron donor (such as silanes) is used during the polymerization, obtained polypropylene may have an isotacticity of up to 98% and a broad molecular weight distribution.

In the 1,3-diether compounds having the general formula (I) useful in the catalyst components according to the present invention, it is preferred that R^{III} and R^{IV} are bonded each other to form an unsaturated fused ring structure, and hydrogen atoms on said fused ring structure are optionally substituted by one or more groups selected from the group consisting of halogen, optionally halogenated linear or branched C_1 - C_{20} alkyl, optionally halogenated C_3 - C_{20} cycloalkyl, optionally halogenated C_6 - C_{20} aryl, optionally halogenated C_7 - C_{20} alkaryl and

optionally halogenated C₇-C₂₀ aralkyl. More preferably, said 1,3-diether compounds are those compounds represented by general formula (II),



Still more preferably, said 1,3-diether compounds are those compounds represented by general formula (III),



In above formulae (II) and (III), R are identical or different, and are selected from the group consisting of hydrogen, halogen, optionally halogenated linear or branched C₁-C₂₀ alkyl, optionally halogenated C₃-C₂₀ cycloalkyl, optionally halogenated C₆-C₂₀ aryl, optionally halogenated C₇-C₂₀ alkaryl and optionally halogenated C₇-C₂₀ aralkyl;

R₁ are identical or different, and are selected from the group consisting of hydrogen, halogen, optionally halogenated linear or branched C₁-C₂₀ alkyl, optionally halogenated C₃-C₂₀ cycloalkyl, optionally halogenated C₆-C₂₀ aryl, optionally halogenated C₇-C₂₀ alkaryl and optionally halogenated C₇-C₂₀ aralkyl;

R₂ are identical or different, and are selected from the group consisting of optionally halogenated linear or branched C₁-C₂₀ alkyl, optionally halogenated C₃-C₂₀ cycloalkyl, optionally halogenated C₆-C₂₀ aryl, optionally halogenated

C₇-C₂₀ alkaryl and optionally halogenated C₇-C₂₀ aralkyl.

Examples of said 1,3-diether compounds having the general formula (I) include:

2-(2-ethylhexyl)-1,3-dimethoxypropane;
2-isopropyl-1,3-dimethoxypropane;
2-butyl-1,3-dimethoxypropane;
2-sec-butyl-1,3-dimethoxypropane;
2-cyclohexyl-1,3-dimethoxypropane;
2-phenyl-1,3-dimethoxypropane;
2-cumyl-1,3-dimethoxypropane;
2-(2-phenylethyl)-1,3-dimethoxypropane;
2-(2-cyclohexylethyl)-1,3-dimethoxypropane;
2-(p-chlorophenyl)-1,3-dimethoxypropane;
2-(diphenylmethyl)-1,3-dimethoxypropane;
2-(1-naphthyl)-1,3-dimethoxypropane;
2-(2-fluorophenyl)-1,3-dimethoxypropane;
2-(1-decahydronaphthyl)-1,3-dimethoxypropane;
2-(p-tert-butylphenyl)-1,3-dimethoxypropane;
2,2-dicyclohexyl-1,3-dimethoxypropane;
2,2-dicyclopentyl-1,3-dimethoxypropane;
2,2-diethyl-1,3-dimethoxypropane;
2,2-dipropyl-1,3-dimethoxypropane;
2,2-diisopropyl-1,3-dimethoxypropane;
2,2-dibutyl-1,3-dimethoxypropane;
2-methyl-2-propyl-1,3-dimethoxypropane;
2-methyl-2-benzyl-1,3-dimethoxypropane;
2-ethyl-2-methyl-1,3-dimethoxypropane;
2-isopropyl-2-methyl-1,3-dimethoxypropane;
2-methyl-2-phenyl-1,3-dimethoxypropane;

2-methyl-2-cyclohexyl-1,3-dimethoxypropane;
2,2-bis(p-chlorophenyl)-1,3-dimethoxypropane;
2,2-bis(2-cyclohexylethyl)-1,3-dimethoxypropane;
2-isobutyl-2-methyl-1,3-dimethoxypropane;
2-methyl-2-(2-ethylhexyl)-1,3-dimethoxypropane;
2,2-diisobutyl-1,3-dimethoxypropane;
2,2-diphenyl-1,3-dimethoxypropane;
2,2-dibenzyl-1,3-dimethoxypropane;
2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane;
2-isobutyl-2-isopropyl-1,3-dimethoxypropane;
2-isopropyl-2-(1-methylbutyl)-1,3-dimethoxypropane;
2-(1-methylbutyl)-2-sec-butyl-1,3-dimethoxypropane;
2,2-di-sec-butyl-1,3-dimethoxypropane;
2,2-di-tert-butyl-1,3-dimethoxypropane;
2,2-di-neopentyl-1,3-dimethoxypropane;
2-isopentyl-2-isopropyl-1,3-dimethoxypropane;
2-isopropyl-2-phenyl-1,3-dimethoxypropane;
2-sec-butyl-2-phenyl-1,3-dimethoxypropane;
2-isopropyl-2-benzyl-1,3-dimethoxypropane;
2-sec-butyl-2-benzyl-1,3-dimethoxypropane;
2-benzyl-2-phenyl-1,3-dimethoxypropane;
2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane;
2-sec-butyl-2-cyclopentyl-1,3-dimethoxypropane;
2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane;
2-sec-butyl-2-cyclohexyl-1,3-dimethoxypropane;
2-isopropyl-2-sec-butyl-1,3-dimethoxypropane;
2-cyclohexylmethyl-2-cyclohexyl-1,3-dimethoxypropane;
1,1-bis(methoxymethyl)-cyclopentadiene;
1,1-bis(methoxymethyl)-2,3,4,5-tetramethylcyclopentadiene;

1,1-bis(methoxymethyl)-2,3,4,5-tetraphenylcyclopentadiene;
1,1-bis(methoxymethyl)-2,3,4,5-tetrafluorocyclopentadiene;
1,1-bis(methoxymethyl)-3,4-dicyclopentylcyclopentadiene;
1,1-bis(methoxymethyl)indene;
1,1-bis(methoxymethyl)-2,3-dimethoxyindene;
1,1-bis(methoxymethyl)-4,5,6,7-tetrafluoroindene;
1,1-bis(methoxymethyl)-2,3,6,7-tetrafluoroindene;
1,1-bis(methoxymethyl)-4,7-dimethylindene;
1,1-bis(methoxymethyl)-3,6-dimethylindene;
1,1-bis(methoxymethyl)-4-phenylindene;
1,1-bis(methoxymethyl)-4-phenyl-2-methylindene;
1,1-bis(methoxymethyl)-4-cyclohexylindene;
1,1-bis(methoxymethyl)-7-(3,3,3-trifluoropropyl)indene;
1,1-bis(methoxymethyl)-7-trimethylsilylindene;
1,1-bis(methoxymethyl)-7-trifluoromethylindene;
1,1-bis(methoxymethyl)-4,7-dimethyl-4,5,6,7-tetrahydroindene;
1,1-bis(methoxymethyl)-7-methylindene;
1,1-bis(methoxymethyl)-7-cyclopentylindene;
1,1-bis(methoxymethyl)-7-isopropylindene;
1,1-bis(methoxymethyl)-7-cyclohexylindene;
1,1-bis(methoxymethyl)-7-tert-butylindene;
1,1-bis(methoxymethyl)-2-methyl-7-tert-butylindene;
1,1-bis(methoxymethyl)-7-phenylindene;
1,1-bis(methoxymethyl)-2-phenylindene;
9,9-bis(methoxymethyl)fluorene;
9,9-bis(methoxymethyl)-2,3,6,7-tetramethylfluorene;
9,9-bis(methoxymethyl)-2,3,4,5,6,7-hexafluorofluorene;
9,9-bis(methoxymethyl)-2,3-benzoindene;
9,9-bis(methoxymethyl)-2,3,6,7-dibenzoindene;

9,9-bis(methoxymethyl)-2,7-dicyclopentylfluorene;
9,9-bis(methoxymethyl)-1,8-dichlorofluorene;
9,9-bis(methoxymethyl)-2,7-dicyclohexylfluorene;
9,9-bis(methoxymethyl)-1,8-difluorofluorene;
9,9-bis(methoxymethyl)-1,2,3,4-tetrahydrofluorene;
9,9-bis(methoxymethyl)-1,2,3,4,5,6,7,8-octahydrofluorene;
9,9-bis(methoxymethyl)-4-tert-butylfluorene;
1,1-bis(1-butoxyethyl)-cyclopentadiene;
1,1-bis(1-isopropoxy-n-propyl)-cyclopentadiene;
1-methoxymethyl-1-(1-methoxyethyl)-2,3,4,5-tetramethylcyclopentadiene;
1,1-bis(alpha-methoxybenzyl)indene;
1,1-bis(phenoxyethyl)indene;
1,1-bis(1-methoxyethyl)-5,6-dichloroindene;
1,1-bis(phenoxyethyl)-3,6-dicyclohexylindene;
1-methoxymethyl-1-(1-methoxyethyl)-7-tert-butylindene;
1,1-bis[2-(2-methoxypropyl)]-2-methylindene;
9,9-bis(alpha-methoxybenzyl)fluorene;
9,9-bis(1-isopropoxy-n-butyl)-4,5-diphenylfluorene;
9,9-bis(1-methoxyethyl)fluorene;
9-(methoxymethyl)-9-(1-methoxyethyl)-2,3,6,7-tetrafluorofluorene;
9-(methoxymethyl)-9-(pentoxymethyl)fluorene;
9-(methoxymethyl)-9-(ethoxymethyl)fluorene;
9-(methoxymethyl)-9-(1-methoxyethyl)fluorene;
9-(methoxymethyl)-9-[2-(2-methoxypropyl)]fluorene;
1,1-bis(methoxymethyl)-2,5-cyclohexadiene;
1,1-bis(methoxymethyl)benzonaphthalene;
7,7-bis(methoxymethyl)-2,5-norbornadiene;
9,9-bis(methoxymethyl)-1,4-methanedihydronaphthalene;
9,9-bis(methoxymethyl)-9,10-dihydroanthracene;

1,1-bis(methoxymethyl)-1,2-dihydroanthracene;
4,4-bis(methoxymethyl)-1-phenyl-1,4-dihydronaphthalene;
4,4-bis(methoxymethyl)-1-phenyl-3,4-dihydronaphthalene;
5,5-bis(methoxymethyl)-1,3,6-cycloheptatriene,
and the like.

According to a specific embodiment, the solid catalyst component according to the present invention can be prepared as follows:

(i) Preparation of magnesium chloride solution:

The magnesium chloride solution can be prepared by some methods known in the art. For instance, the magnesium chloride solution can be prepared utilizing a dissolving system of magnesium chloride as disclosed in US4784983 and US4861847.

In the present invention, the magnesium chloride solution can be preferably prepared as follows:

To a reactor equipped with a stirrer, an alcohol or a mixture of two or more alcohols is added, optionally followed by further addition of ether(s) or ester(s). Anhydrous magnesium chloride is then added and is dissolved with heating, wherein molar ratio of the alcohol(s) to magnesium chloride is in a range of from 3:1 to 50:1, and molar ratio of the ether(s) or ester(s) to magnesium chloride is in a range of from 0:1 to 20:1. The dissolution of magnesium chloride can be carried out in presence of an inert organic solvent, with the amount of the inert solvent used being in a range of from 0 to 20 ml per gram of $MgCl_2$.

(ii) Preparation of spheric $MgCl_2/SiO_2$ composite carrier

Silica, preferably fumed silica having an average particle size of less than 10 microns is added to the magnesium chloride solution at an amount of from 0.1 to 2.0 grams of silica with respect to one gram of magnesium chloride. Then the mixture is stirred for from 0.5 to 3 hours at a temperature of from 10 to 100 °C to form a slurry. Next, spray drying is carried out by passing the slurry together with an inert drying gas through a spray dryer to obtain spheric $MgCl_2/SiO_2$ composite

carrier having an average particle size of from 5 to 60 microns. Inlet temperature of the spray dryer is controlled at from 80 to 300 °C, and outlet temperature of the spray dryer is controlled at from 50 to 200 °C. Typically, the composite carrier has a composition of

MgCl₂: from 20% to 60% (by weight);
SiO₂: from 10% to 60% (by weight);
Alcohol(s): from 5% to 40% (by weight);
Ether(s) or ester(s): from 0 to 20% (by weight);
Inert solvent(s): less than 5% (by weight).

(iii) Preparation of solid catalyst component

The above-obtained spheric carrier is suspended in cooled TiCl₄ with TiCl₄ being used at an amount of from 12 to 16 ml per gram of the carrier. The suspension is slowly heated to a temperature of from 100 to 120 °C over a period of from 1 to 3 hours, while an internal electron donor compound is added at an amount of from 0.05 to 0.25 mole with respect to one mole of magnesium chloride during heating. Filtration is performed after reacting for 1 to 2 hours. Optionally, an amount of TiCl₄ is further added, and the mixture is held at 120 °C for 1 to 2 hours, followed by filtering out the liquid. Residual solid is washed with an inert solvent such as hexane, then the solid is dried at a temperature of from 30 to 50 °C under vacuum to give a solid catalyst component according to the present invention.

In the third aspect, the present invention relates to a catalyst for propylene polymerization, comprising reaction product of:

- (i) the solid catalyst component according to the present invention (active component);
- (ii) alkyl aluminium compound component, which is represented by formula AlR³_nX_{3-n}, in which R³ are identical or different, and are linear, branched, or cyclic alkyl having 1 to 20 carbon atoms, X is halogen, n=1, 2 or 3, with triethyl aluminium, triisobutyl aluminium, tri-n-butyl aluminium, tri-n-hexyl aluminium, tri-n-octyl aluminium, alkyl aluminium chloride such as diethyl aluminium chloride,

and the like being preferred, and the alkyl aluminium compound being used alone or in combination; and

(iii)optionally, an external electron donor compound, for example, mono- or multi-functional carboxylic acids, carboxylic acid anhydrides and carboxylic acid esters, ketones, ethers, alcohols, lactones, organo phosphorus compounds and organosilicone compounds, with organosilicone compounds, such as those represented by formula $R^4_nSi(OR^5)_{4-n}$ in which n is in a range of from 0 to 3 inclusive, R^4 and R^5 are identical or different, and are alkyl, cycloalkyl, aryl or haloalkyl, R^4 can also be halogen or hydrogen atom, being preferred.

In many cases, for example in the case of using aforementioned esters of aliphatic polycarboxylic acid or esters of aromatic carboxylic acid as internal electron donor, use of an external electron donor is very important.

For instance, in the case of using an aforementioned organosilicone compound as external electron donor, ratio of solid catalyst component (i) to alkyl aluminium compound component (ii) to external electron donor component (iii) is in a range of 1:5 to 1000:0 to 500, calculated on molar basis of titanium, aluminium and silicone.

It is possible to contact the component (ii) and the optional component (iii), separately or as a mixture of said two components, with the active component.

The term "polymerization" as used herein intends to include homopolymerization and copolymerization. The term "polymer" as used herein intends to include homopolymer, copolymer and terpolymer.

The catalysts of the invention can be used in the homopolymerization of propylene and copolymerization of propylene and alpha-olefins such as ethylene, 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene, and optionally diolefin. In particular, said catalysts can be used to produce, such as, the following products: elastomeric copolymer of ethylene and propylene, and elastomeric terpolymers of ethylene and propylene as well as diolefins at a small porportion, wherein the weight content of the units derived from ethylene is between about 30% and 70%;

isotactic polypropylene and crystalline copolymer of propylene and ethylene and/or other alpha-olefins, wherein the content of the units derived from propylene is higher than 85% by weight (random copolymer); impact resistant propylene polymer, which are produced by sequential polymerization of propylene and the mixture of propylene and ethylene, with the content of ethylene being up to 40% by weight; copolymer of propylene and 1-butene, containing a great amount, such as from 10 to 40 percent by weight, of units derived from 1-butene.

The catalysts of the invention can be used in various known olefin polymerization processes, including continuous polymerization and batch polymerization. For instance, the polymerization can be carried out in slurry with inert hydrocarbon solvents as diluent or in bulk with liquid monomers, such as propylene, as reaction media. Alternatively, the polymerization may be carried out in gas phase in one or more fluidized-bed or mechanically agitated bed reactors.

The polymerization reaction is generally carried out at a temperature of from 0 to 150°C, typically from 20 to 120°C, more typically from 40 to 100°C. When the polymerization is carried out in gas phase, operation pressure is usually in a range of from 0.5 to 10 MPa (absolute pressure, the same hereinafter), preferably from 1 to 5 MPa. The operation pressure in bulk polymerization is usually in a range of from 1 to 6 MPa, preferably from 1.5 to 4 MPa. Hydrogen or other compounds which act as chain-transfer agent can be used to control the molecular weight of polymers.

Compared with the technique of directly preparing a solid catalyst component through spray drying as disclosed in US4376062, the present invention can control the composition of solid catalyst product more well, in particular, the present invention can expediently adjust content and kind of the internal electron donor contained in said solid catalyst component, and this is important for ensuring higher stereospecificity of the catalysts according to the present invention. Furthermore, since the catalyst according to the present invention comprises silica having primary particles with very small particle size, and exhibits very high

polymerization activity, it can more effectively avoid the occurrence of fish eye phenomenon than those prepared by impregnating process when used in production of a film grade product. Moreover, since the catalyst according to the present invention comprises particles with plenty of micropore structure, and possesses homogeneously distributed active component, it exhibits good copolymerization performance so that it can be used to prepare high impact resistant propylene copolymer having high ethylene content, and is suitable for gas phase process of propylene polymerization. The catalyst according to the present invention is particularly suitable for gas phase process of propylene polymerization.

Embodiments of the Invention

The following examples further describe the invention, but do not make limitation to the invention in any way.

Example 1

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely replaced with N₂, 34.5ml of ethanol, 18.5ml of n-butanol and 32.4ml of THF were added successively. 9.5g of anhydrous magnesium chloride was added with stirring while controlling temperature inside the glass reactor not raising rapidly, then the temperature inside the glass reactor was slowly raised to about 60 °C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved, the system was held at that temperature for further 2.5 hours to form a magnesium chloride solution.

2. Preparation of composite carrier

To above solution was added 6g of fumed silica (TS-610 with particle size in a range of from 0.02 to 0.1 micron, available from Cabot Corporation, the same hereinafter). Then the mixture was stirred for 1 hour at room temperature to form a

slurry. Next, spray drying was carried out in a spray dryer with inlet temperature of the spray dryer being controlled at 200 °C and outlet temperature of the spray dryer being controlled at 130 °C, to form spheric composite carrier having an average particle size of about 1.7 microns. The composite carrier was found to have a composition of MgCl₂: 43.3%; SiO₂: 26.5%; ethanol: 11.2%; n-butanol: 14.7%, THF: 4.2%, calculated on weight basis.

3. Preparation of solid catalyst component

9.1g of above-obtained composite carrier was slowly added to 100ml of TiCl₄ pre-cooled to 0 °C. The mixture was heated to 40 °C over one hour, and 1.0ml of di-n-butyl phthalate (DNBP) was added at said temperature. Then the mixture was heated to 100 °C over 0.5 hour and held at that temperature for 2 hours, followed by filtering out mother liquid. Additional 100ml of TiCl₄ was added to the reactor, and the content was heated to 120 °C over 0.5 hour and held at that temperature for 1 hour, followed by filtering out mother liquid. Residual solid was washed with hexane at 60 °C for 5 times with the amount of hexane used being 60ml at each time. Finally, the solid was dried to give a solid catalyst component.

Propylene polymerization:

To a 5L autoclave, which had been purged with propylene gas at 70 °C for one hour, were introduced with 5ml of 0.5mmol/ml solution of AlEt₃ in hexane, 1ml of 0.1mmol/ml solution of cyclohexylmethyldimethoxysilane (CHMMS) in hexane, 8.5mg of above-prepared solid spheric catalyst component in 10ml of dried hexane, and 1.7NL of hydrogen, followed by introduction of 1.5Kg of liquid propylene. The reactor was heated to 70°C with stirring over 5 minutes, and the polymerization was performed at that temperature and autogenous pressure for 2 hours. After stopping the stirrer, un-polymerized propylene monomer was removed, and the temperature inside the reactor was reduced to room temperature.

310g of PP powder was obtained. Isotacticity index (I.I.) of the polypropylene was found as 96.0%, melt index (M.I.) was found as 5.1g/10min, catalyst activity was 36.5KgPP per gram of solid catalyst component, and bulk density of the

polymer was 0.42g/ml.

Example 2

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely replaced with N₂, 34.5ml of ethanol and 45.5ml of isopropanol were added successively. 9.5g of anhydrous magnesium chloride was added with stirring while controlling temperature inside the glass reactor not raising rapidly, then the temperature inside the glass reactor was slowly raised to about 75 °C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved, the system was held at that temperature for further 2.5 hours to form a magnesium chloride solution.

2. Preparation of composite carrier

To above solution was added 5g of fumed silica. Then the mixture was stirred for 1 hour at room temperature to form a slurry. Next, spray drying was carried out in a spray dryer with inlet temperature of the spray dryer being controlled at 190 °C and outlet temperature of the spray dryer being controlled at 110 °C, to form spheric composite carrier having an average particle size of about 19 microns. The composite carrier was found to have a composition of MgCl₂: 45.7%; SiO₂: 24.1%; ethanol: 13.3%; isopropanol: 16.7%, calculated on weight basis.

3. Preparation of solid catalyst component

A solid catalyst component was prepared according to the procedure as described in Example 1.

Propylene polymerization:

The procedure of propylene polymerization was same as that described in Example 1. Catalyst activity was 38.0Kg of PP per gram of solid catalyst component, isotacticity index (I.I.) of the obtained polypropylene was found as 96.6%, melt index (M.I.) was found as 5.2g/10min, and bulk density of the polymer was 0.43g/ml.

Example 3

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely replaced with N₂, 23.0ml of ethanol and 36.0ml of n-butanol were added successively. 9.5g of anhydrous magnesium chloride was added with stirring while controlling temperature inside the glass reactor not raising rapidly, then the temperature inside the glass reactor was slowly raised to about 70 °C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved, the system was held at that temperature for further 2.5 hours to form magnesium chloride solution.

2. Preparation of composite carrier

The procedure described in Example 1 was repeated to give spheric composite carrier having an average particle size of about 17 microns. The composite carrier was found to have a composition of MgCl₂: 47.5%; SiO₂: 23.2%; ethanol: 5.9%; n-butanol: 23.5%, calculated on weight basis.

3. Preparation of solid catalyst component

A solid catalyst component was prepared according to the procedure as described in Example 1.

Propylene polymerization:

The procedure of propylene polymerization was same as that described in Example 1. Catalyst activity was 25.1Kg of PP per gram of solid catalyst component, isotacticity index (I.I.) of the obtained polypropylene was found as 96.8%, melt index (M.I.) was found as 3.0g/10min, and bulk density of the polymer was 0.42g/ml.

Example 4

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely

replaced with N_2 , 46.0ml of ethanol, 15.6ml of epoxy chloropropane and 32.4ml of THF were added successively. 9.5g of anhydrous magnesium chloride was added with stirring while controlling temperature inside the glass reactor not raising rapidly, then the temperature inside the glass reactor was slowly raised to about 60 °C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved, the system was held at that temperature for further 2.5 hours to form magnesium chloride solution.

2.Preparation of composite carrier

The procedure described in Example 1 was repeated to prepare spheric composite carrier having an average particle size of about 18 microns. The composite carrier was found to have a composition of $MgCl_2$: 48.6%; SiO_2 : 25.2%; ethanol: 16.8%; epoxy chloropropane: 3.6%, THF: 5.9%, calculated on weight basis.

3.Preparation of solid catalyst component

A solid catalyst component was prepared according to the procedure as described in Example 1.

Propylene polymerization:

The procedure of propylene polymerization was same as that described in Example 1. Catalyst activity was 11.6Kg of PP per gram of solid catalyst component, isotacticity index (I.I.) of the obtained polypropylene was found as 96.5%, melt index (M.I.) was found as 3.6g/10min, and bulk density of the polymer was 0.43g/ml.

Example 5

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely replaced with N_2 , 34.5ml of ethanol and 45.5ml of isopropanol were added successively. 9.5g of anhydrous magnesium chloride was added with stirring while controlling temperature inside the glass reactor not raising rapidly, then the

temperature inside the glass reactor was slowly raised to about 75 °C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved, 0.2ml of ethyl benzoate was added to the solution, then the system was held at that temperature for further 2.5 hours to form magnesium chloride solution.

2.Preparation of composite carrier

The procedure described in Example 2 was repeated to prepare spheric composite carrier having an average particle size of about 18 microns. The composite carrier was found to have a composition of MgCl₂: 46.1%; SiO₂: 24.3%; ethanol: 13.3%; isopropanol: 16.3%, ethyl benzoate: 0.02%, calculated on weight basis.

3.Preparation of solid catalyst component

A solid catalyst component was prepared according to the procedure as described in Example 1.

Propylene polymerization:

The procedure of propylene polymerization was same as that described in Example 1. Catalyst activity was 42.0Kg of PP per gram of solid catalyst component, isotacticity index (I.I.) of the obtained polypropylene was found as 97.4%, melt index (M.I.) was found as 3.6g/10min, and bulk density of the polymer was 0.43g/ml.

Example 6

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely replaced with N₂, 80ml of toluene, 8.2ml of tributyl phosphate, 7.8ml of epoxy chloropropane and 4.8g of anhydrous magnesium chloride were added successively. Then the temperature inside the glass reactor was slowly raised to about 55°C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved, the system was held at

that temperature for further 2.5 hours to form a magnesium chloride solution.

2.Preparation of composite carrier

To above solution was added 3.5g of fumed silica. Then the mixture was stirred for 1 hour at room temperature to form a slurry. Next, spray drying was carried out in a spray dryer with inlet temperature of the spray dryer being controlled at 200 °C and outlet temperature of the spray dryer being controlled at 130 °C, to prepare a spheric composite carrier having an average particle size of about 18 microns.

3.Preparation of solid catalyst component

A solid catalyst component was prepared according to the procedure as described in Example 1.

Propylene polymerization:

The procedure of propylene polymerization was same as that described in Example 1. Catalyst activity was 26.0Kg of PP per gram of solid catalyst component, isotacticity index (I.I.) of the obtained polypropylene was found as 96.5%, melt index (M.I.) was found as 3.1g/10min, and bulk density of the polymer was 0.41g/ml.

Example 7

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely replaced with N₂, 150ml of ethanol and 9.5g of anhydrous magnesium chloride were added successively. Then the temperature inside the glass reactor was slowly raised to about 50 °C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved, the system was held at that temperature for further 2.5 hours to form a magnesium chloride solution.

2.Preparation of composite carrier

To above solution was added 6g of fumed silica. Then the mixture was stirred

for 1 hour at room temperature to form a slurry. Next, spray drying was carried out in a spray dryer with inlet temperature of the spray dryer being controlled at 190 °C and outlet temperature of the spray dryer being controlled at 110 °C, to prepare spheric composite carrier having an average particle size of about 16 microns.

3.Preparation of solid catalyst component

A solid catalyst component was prepared according to the procedure as described in Example 1.

Propylene polymerization:

The procedure of propylene polymerization was same as that described in Example 1. Catalyst activity was 23.0Kg of PP per gram of solid catalyst component, isotacticity index (I.I.) of the obtained polypropylene was found as 96.0%, melt index (M.I.) was found as 7.2g/10min, and bulk density of the polymer was 0.42g/ml.

Example 8

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely replaced with N₂, 34.5ml of ethanol, 18.5ml of n-butanol and 32.4ml of THF were added successively. 9.5g of anhydrous magnesium chloride was added with stirring while controlling temperature inside the glass reactor not raising rapidly, then the temperature inside the reactor was slowly raised to about 60 °C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved, the system was held at that temperature for further 2.5 hours to form a magnesium chloride solution.

2.Preparation of composite carrier

To above solution was added 6g of fumed silica. Then the mixture was stirred for 1 hour at room temperature to form a slurry. Next, spray drying was carried out in a spray dryer with inlet temperature of the spray dryer being controlled at 200 °C and outlet temperature of the spray dryer being controlled at 130 °C, to form spheric

composite carrier having an average particle size of about 17 microns.

3.Preparation of catalyst component

9.1g of above-obtained composite carrier was slowly added to 100ml of $TiCl_4$ pre-cooled to 0 °C. The mixture was heated to 40 °C over one hour, and 4.7mmol of 2-isopentyl-2-isopropyl-1,3-dimethoxypropane was added at said temperature. Then the mixture was heated to 100 °C over 0.5 hour and held at that temperature for 2 hours, followed by filtering out mother liquid. Additional 100ml of $TiCl_4$ was added to the reactor, and the content was heated to 120 °C over 0.5 hour and held at that temperature for 1 hour, followed by filtering out mother liquid. Residual solid was washed with hexane at 60 °C for 5 times with the amount of hexane used being 60ml at each time. Finally, the solid was dried to give a solid catalyst component. In said catalyst component, the content of magnesium was 13.2% by weight, the content of titanium was 3.3% by weight, and the content of 2-isopentyl-2-isopropyl-1,3-dimethoxypropane was 8.8% by weight.

Propylene polymerization:

To a 5L autoclave, which had been purged with propylene gas at 70 °C for one hour, were introduced with 5ml of 0.5mmol/ml solution of $AlEt_3$ in hexane, 1ml of 0.1mmol/ml solution of cyclohexylmethyldimethoxysilane (CHMMS) in hexane, 8.0mg of above-prepared solid spheric catalyst component in 10ml of hexane, and 1.7NL of hydrogen, followed by introduction of 1.5Kg of liquid propylene. The reactor was heated to 70°C with stirring over 5 minutes, and the polymerization was performed at that temperature and autogenous pressure for 2 hours. After stopping the stirrer, un-polymerized propylene monomer was removed, and the temperature inside the reactor was reduced to room temperature.

370g of PP powder was removed from the autoclave. Isotacticity index (I.I.) of the polypropylene was found as 98.0%, melt index (M.I.) was found as 5.1g/10min, and molecular weight distribution (M_w/M_n) was found as 7.1. Catalyst activity was 46.3Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.43g/ml.

Example 9

The preparation of magnesium chloride solution, composite carrier and catalyst component follows the procedure as described in Example 8.

Propylene polymerization was carried out according to the procedure as described in Example 8, except that no external electron donor was added. Catalyst activity was 51.5Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.42g/ml. Isotacticity index (I.I.) of the obtained polypropylene was 94.3%, melt index (M.I.) was 6.2g/10min, and molecular weight distribution (Mw/Mn) was 7.0.

Example 10

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely replaced with N₂, 34.5ml of ethanol and 45.5ml of isopropanol were added successively. 9.5g of anhydrous magnesium chloride was added with stirring while controlling temperature inside the glass reactor not raising rapidly, then the temperature inside the glass reactor was slowly raised to about 75 °C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved, the system was held at that temperature for further 2.5 hours to form a magnesium chloride solution.

2. Preparation of composite carrier

To above solution was added 5g of fumed silica. Then the mixture was stirred for 1 hour at room temperature to form a slurry. Next, spray drying was carried out in a spray dryer with inlet temperature being controlled at 190 °C and outlet temperature being controlled at 110 °C, to form a spheric composite carrier having an average particle size of about 19 microns.

3. Preparation of solid catalyst component

A solid catalyst component was prepared according to the procedure as

described in Example 8.

Propylene polymerization:

The procedure of propylene polymerization was same as that described in Example 8. Catalyst activity was 54.0Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.42g/ml. Isotacticity index (I.I.) of the obtained polypropylene was found as 97.6%, melt index (M.I.) was found as 5.2g/10min, and molecular weight distribution (Mw/Mn) was 7.3.

Example 11

The preparation of magnesium chloride solution, composite carrier and catalyst component follows the procedure as described in Example 10.

Propylene polymerization was carried out according to the procedure as described in Example 10, except that no external electron donor was added. Catalyst activity was 60.0Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.40g/ml. Isotacticity index (I.I.) of the obtained polypropylene was found as 93.8%, melt index (M.I.) was found as 6.3g/10min, and molecular weight distribution (Mw/Mn) was 7.3.

Example 12

Example 8 was repeated, except that 9,9-bis(methoxymethyl)fluorene was used to substitute 2-isopentyl-2-isopropyl-1,3-dimethoxypropane.

Catalyst activity was 54.2Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.43g/ml. Isotacticity index (I.I.) of the obtained polypropylene was found as 97.8%, melt index (M.I.) was found as 4.0g/10min, and molecular weight distribution (Mw/Mn) was 7.6.

Example 13

Example 12 was repeated, except that no external electron donor was added during propylene polymerization.

Catalyst activity was 62.4Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.40g/ml. Isotacticity index (I.I.) of the obtained polypropylene was found as 92.8%, melt index (M.I.) was found as 5.3g/10min, and molecular weight distribution (Mw/Mn) was 7.4.

Example 14

Example 10 was repeated, except that 9,9-bis(methoxymethyl)fluorene was used to substitute 2-isopentyl-2-isopropyl-1,3-dimethoxypropane.

Catalyst activity was 58.6Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.43g/ml. Isotacticity index (I.I.) of the obtained polypropylene was found as 97.8%, melt index (M.I.) was found as 4.0g/10min, and molecular weight distribution (Mw/Mn) was 7.4.

Example 15

Example 14 was repeated, except that no external electron donor was added during propylene polymerization.

Catalyst activity was 64.3Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.40g/ml. Isotacticity index (I.I.) of the obtained polypropylene was found as 93.0%, melt index (M.I.) was found as 5.8g/10min, and molecular weight distribution (Mw/Mn) was 7.3.

Example 16

1. Preparation of magnesium chloride solution:

To a 350ml glass reactor equipped with a stirrer, which was completely replaced with N₂, 200ml of ethanol was added. 9.5g of anhydrous magnesium chloride was added with stirring while controlling temperature inside the glass reactor not raising rapidly, then the temperature inside the glass reactor was slowly raised to about 60 °C, and the anhydrous magnesium chloride was well dissolved with stirring. After the anhydrous magnesium chloride was substantially dissolved,

the system was held at that temperature for further 2.5 hours to form a magnesium chloride solution.

2.Preparation of composite carrier

To above solution was added 6g of fumed silica. Then the mixture was stirred for 1 hour at room temperature to form a slurry. Next, spray drying was carried out in a spray dryer with inlet temperature being controlled at 200 °C and outlet temperature being controlled at 130 °C, to prepare a spheric composite carrier having an average particle size of about 18 microns.

3.Preparation of solid catalyst component

A solid catalyst component was prepared according to the procedure as described in Example 12.

Propylene polymerization:

The procedure of propylene polymerization was same as that described in Example 8. Catalyst activity was 43.6Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.42g/ml. Isotacticity index (I.I.) of the obtained polypropylene was found as 97.0%, melt index (M.I.) was found as 5.6g/10min, and molecular weight distribution (Mw/Mn) was 7.1.

Comparative Example 1

Preparation of catalyst component (no composite carrier of the present invention was used):

To a reactor, which was completely replaced with high pure N₂, were added successively 0.05mol of anhydrous magnesium chloride, 95ml of toluene, 0.05mol of epoxy chloropropane (ECP), and 0.046mol of tributyl phosphate (TBP). The mixture was heated to 50°C with stirring and held at the temperature for 2.5 hours to dissolve the solid completely, then 0.0095mol of phthalic anhydride was added, and the mixture was held at the temperature for further one hour. The solution was cooled to -25°C and 56ml of TiCl₄ was dropwise added over one hour, then the reaction mixture was slowly heated to 80°C. Solid was gradually precipitated

during the heating. To the system was added 2g of 9,9-bis(methoxymethyl)fluorene, and the reaction was held at that temperature for further one hour. After filtration, the residue was washed with 100mlx2 of toluene for two times. A brownish solid precipitate was obtained. The resulting solid precipitate was treated with 60ml of toluene and 40ml of $TiCl_4$ at 90°C for 2 hours, and after removing the supernatant, the residue was treated again. After removing the supernatant, the residue was washed with 100mlx3 of toluene at 110 °C for three times, and 100mlx4 of hexane for four times, to yield a solid catalyst component.

Propylene polymerization:

The procedure of propylene polymerization was same as that described in Example 9, except that polymerization time was 1 hour. Catalyst activity was 53.6Kg of PP per gram of solid catalyst component, and bulk density of the polymer was 0.44g/ml. Isotacticity index (I.I.) of the obtained polypropylene was found as 98.8%, melt index (M.I.) was found as 4.5g/10min, and molecular weight distribution (Mw/Mn) was 3.6.

It can be seen from above Examples that when used in propylene polymerization, a catalyst prepared by employing the composite carrier according to the present invention, the 1,3-diether compound and titanium compound as essential components not only exhibits high polymerization activity and high bulk density of polymer but remains characteristics of catalyst components using a 1,3-diether compound as internal electron donor, that is, the catalyst components have good response to hydrogen and an external electron donor is not necessary. In addition, the obtained polymer has a broader molecular weight distribution with Mw/Mn being larger than 7. If a catalyst is prepared by employing 1,3-diether compounds as internal electron donor yet no composite carrier according to the present invention, the obtained polymer has a narrower molecular weight distribution as shown in Comparative Example.